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13. ABSTRACT *(Maximum 200 words)*

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Low dimensional inorganic semiconductor systems have been of much scientific and technological interest in the past 25 years (*1-3*). Compared to bulk semiconductors, low dimensional semiconductors exhibit novel or modified electronic and optical properties due to spatial confinement of charge carriers or excitons (*1-3*). Increased exciton binding energy, enhanced oscillator strengths, large Stark shifts, and enhanced optical nonlinearities in low dimensional semiconductors have led to device applications such as diode lasers, Stark effect optical modulators, self-electrooptic effect devices, optical waveguide switches, and cavity-less nonlinear optical bistability (*1-3*). Organic semiconductors with reduced dimensionality are also of growing interest owing to their expected unique features compared to the corresponding inorganic semiconductors (*4-22*). Defect-free heterostructures can be more readily fabricated due to the weak Van der Waals interactions between organic molecules. The smaller dielectric constant of organic molecules and polymers [~3-4] compared to inorganic semiconductors [>10] could result in strong Coulomb interactions between electrons and holes, leading to strong excitonic effects and large exciton binding energies [~0.5-1.0 eV]. In spite of the many theoretical studies which have predicted quantum confinement effects in heterostructured organic semiconductors (*9-13*), clear experimental observation of such effects was not reported until recently (*5,6, 19-22*). One major experimental difficulty is the rather small exciton Bohr radii (a_B) in bulk organic semiconductors ($a_B \sim 1.0$-2.0 nm) which places severe limitations on suitable techniques for preparing the nanoscale structures(*5,6,18,23*).

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Layered organic quantum-well heterostructures, which are stacks of alternating thin films of different organic dye molecules, have been prepared by ultrahigh vacuum organic molecular beam deposition (OMBD) technique (4-7). Layered nanostructures of naphthalene and perylene derivatives grown by OMBD have been shown to exhibit the characteristics of multiple quantum wells (MQWs) with one-dimensional exciton confinement (4-6). The resulting two-dimensional excitons in such OMBD grown crystalline MQWs have been shown to be spatially extended (Wannier-like), almost spherical with Bohr radii of 1.3 nm, and to have binding energies as large as 150 meV which are larger than usually found in inorganic MQWs by an order of magnitude (5,6). Other approaches to layered organic semiconductor nanostructures, such as sequential electrochemical polymerization, have also been explored (8). Semiconducting polymer heterostructures consisting of alternating layers of polythiophene and polypyrrole have been successfully prepared (8). However, the characteristic new discrete excitonic features in absorption or excitation spectra commonly observed in inorganic semiconductor MQWs and superlattices (2,3) were not observed in the organic MQWs (5,6,8).

It is expected that organic semiconductor systems in which the motion of charges or excitons is confined to one or zero dimension (quantum wires or quantum boxes) will provide materials with even more remarkable new properties compared to layered quantum-well heterostructures. Many theoretical calculations have thus investigated quantum confinement effects in block conjugated

copolymer chains (9-13). Theoretical studies of polydiacetylene-polyacetylene-polydiacetylene triblock heterostructures led to the prediction of results similar to those of multiple quantum wells in inorganic low dimensional semiconductors. Discrete split-off exciton states as well as localization of electronic states were predicted(9, 10).

Theoretical studies of various aspects of the electronic and excitonic properties of quasi-one-dimensional semiconducting polymer superlattices which are periodic copolymers $(-A_mB_n-)_x$ have been reported(11-13). Electronic localization phenomena, including split-off subbands and the number of subbands in a potential well were investigated as a function of both the well width and the barrier width (11). The electronic structure was systematically studied as a function of copolymer composition and block sizes A_m and B_n (12). Recent calculations of multiblock copolymer chains showed that alternation of sufficiently long sequences of a lower energy gap polymer (B_n) with those of a higher gap one (A_m) can result in electron confinement in the segments of the chain with lower gap (13). However, the few prior experimental attempts to synthesize such block conjugated copolymers did not produce materials with evidence of quantum size effects (14,15). The experimental studies on conjugated copolymers $(-A_mB_n-)_x$, where the segment lengths were relatively short (m=2-3, n=2-6), could not clearly test the predicted spatial confinement effects (14,15).

Thin films of conjugated Schiff base polymers of chart 1 have been prepared by chemical vapor polymerization of terephthaldehyde and various aromatic diamines (16). Insertion of —O—, —S—, and —CH$_2$— linkages into the parent conjugated polymer poly(1,4-phenylenemethylidynetrilo-1,4-phenylenenitrilomethylidyne) (PPI) was claimed to result in the formation of quantum dot sequences in the chain (16). These authors regarded conjugated polymers such as PPI as "natural quantum wires" and the ether–, thio–, and methylene–linked polymers in chart 1 as quantum-well structures. However, no concrete evidence of quantum confinement effects in the vapor deposited polymer thin films was presented (16). In fact, similar conjugated Schiff base polymers have been chemically synthesized and their electronic structures and nonlinear optical properties extensively investigated in our laboratory (17). These is no conceptual or physical basis for regarding thin films of these polymers (chart 1) as quantum-well structures.

Recently, we reported a self-assembly approach to preparing semiconducting polymer quantum boxes and quantum wires and the first experimental observation of the discrete exciton states in a low dimensional organic semiconductor (19-22). Here, we briefly discuss aspects of quantum confinement of excitons in these self-assembled semiconducting polymer heterostructures (19-22). The quantum boxes and wires investigated were prepared from the conjugated homopolymers poly(benzobisthiazole-1,4-

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phenylene)(PBZT) and poly(2,5-benzoxazole)(2,5-PBO) and triblock copolymer poly(2,5-benzoxazole)-*block*-poly(benzobisthiazole-1,4-phenylene)-*block*-poly(2,5-benzoxazole) which was denoted TBA (*18*). The symmetric $A_nB_mA_n$ triblock copolymer TBA has a middle PBZT block and two outer 2,5-PBO blocks. The homopolymers PBZT and 2,5-PBO have energy gaps, based on absorption band edges, of 2.48 eV and 3.24 eV, respectively (*18*). Thus, the PBZT block of TBA represents a quantum well and the 2,5-PBO blocks constitute electron potential barriers with a height of $\Delta E_g = E_g^A - E_g^B = 0.76$ eV. However, the as-synthesize triblock copolymer was shown to be microphase separated with consequent aggregation of PBZT blocks (*18*). By blending the triblock copolymer TBA with the higher energy-gap homopolymer (2,5-PBO), self-organized semiconducting polymer heterostructures were obtained in which isolated single chains of the triblock can be obtained. From the known 12.5 Å repeat unit length of PBZT (*18*), quantum boxes could be obtained when compared to the exciton Bohr radius (a_B) of PBZT ($a_B = 13$ Å) (*23*) if the block length of the PBZT in TBA is small (2-9 repeat units). On the other hand, PBZT repeat units of 15 or more in TBA ensures that a quantum wire could be obtained. Our initial studies of these low-dimensional organic semiconductors prepared from block conjugated copolymers have revealed remarkable new phenomena due to quantum confinement effects. Of fundamental interest was the detection of new discrete exciton states which confirmed the low dimensional nature of the excitons

in these semiconducting polymer heterostructures. Additional evidence confirming the quantum confinement of excitons in these semiconducting polymer heterostructures included large enhancements of photoluminescence quantum efficiency, enhanced exciton lifetime, and the exceptional exciton stability with temperature and large electric field (19-22). These results represent the first experimental evidence for the quantum confinements effects theoretically predicted (9-13) in block copolymer heterostructures.

In this paper, we report quantum confinement effects in thin films of semiconducting polymer heterostructures prepared by self-organization in blends of a new ABA triblock copolymer with its parent homopolymer A. The new triblock copolymer, poly(2,5-benzoxazole)-*block* -poly(benzobisthiazole-2-hydroxy-1,4-phenylene)-*block* -poly(2,5-benzoxazole) which is denoted TBC (Figure 1), was synthesized, characterized, and used to investigate quantum confinement effects. Copolymer TBC-1 consists of a poly(benzobisthiazole-2-hydroxy-1,4-phenylene) (HPBT) middle block and a poly(2,5-benzoxazole) (2,5-PBO) outer blocks with the composition $A_{20}B_9A_{20}$. The electroactive and photoactive properties of HPBT and 2,5-PBO homopolymers have previously been investigated in our laboratory (18, 24). The optical absorption maxima in the homopolymers HPBT and 2,5-PBO are 450 and 479 nm, and 340 and 355 nm, respectively. The corresponding HOMO-LUMO energy gaps based on absorption band maxima are: $E_g^B = 2.59$ eV (HPBT) and $E_g^A = 3.49$ eV (2,5-

PBO). Thus, the HPBT segment of triblock TBC-1 chain is expected to form a quantum well while the 2,5-PBO blocks form electron potential barriers with ΔE_g = 0.90 eV. Thin films of pure triblock copolymer TBC-1 and its binary blends with 2,5-PBO were investigated by optical absorption, photoluminescence (PL), and photoluminescence excitation (PLE) spectroscopies, time-resolved PL decay dynamics as well as picosecond transient absorption spectroscopy. The results show clear evidence of quantum confinement effects in TBC-1/2,5-PBO blend system.

Experimental Section

Materials. 2,5-Diamino-1,4-benzenedithiol (DABDT) (Daychem or TCI) was purified by recrystallization from aqueous HCl as previously reported(*24*). The 2-hydroxyterephthalic acid was prepared from bromoterephthalic acid by copper-catalyzed displacement of bromine reported by Miura *et al.*(*25*). 3-Amino-4-hydroxy benzoic acid (TCI, 97 %) was used as received. Poly(phosphoric acid)(PPA) and 85 % phosphoric acid (ACS reagent grade, Aldrich) were used to prepare 77 % PPA, which was used as the polymerization medium. Phosphorus pentoxide (Fluka) was used as received.

Synthesis. The triblock copolymer TBC-1 was synthesized by condensation copolymerization in polyphosphoric acid, similar to previously reported procedures(*18*). Carboxylic acid-terminated HPBT block (HOOC-B$_m$-COOH) was synthesized by reacting 2,5-diamino-1,4-benzenedithiol dihydrochloride

(DABDT) with excess 2-hydroxy-terephthalic acid (HTA) in polyphosphoric acid (PPA). The $A_nB_mA_n$ triblock was obtained by copolymerizing HOOC-B_m-COOH with 3-amino-4-hydroxybenzoic acid (AHBA) in PPA. The block lengths m and n were controlled through the stoichiometric ratios of HTA to DABDT and AHBA to HOOC-B_m-COOH. The condensations were designed for a product content of 10 % w/w in 77 % PPA at the completion of reaction. The polymer product was first washed by a large amount of water and then refluxed with water for 24 hours. The typical yield was ~100%. For TBC-1, the average composition is $A_{20}B_9A_{20}$, where A and B are the 2,5-PBO and HPBT repeat units respectively.

Characterization. The ^{1}H NMR spectra were taken at 300 MHz using a General Electric Model QE 300 instrument. Solutions for ^{1}H NMR spectra were prepared in a dry box, using deuterated nitromethane (CD_3NO_2) containing aluminum (III) chloride. FTIR spectra were taken at room temperature using a Nicolet Model 20SXC Fourier transform infrared (FTIR) spectrometer under nitrogen purge. The FTIR samples were in the form of free standing films. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were done using a Du Pont Model 2100 Thermal Analyst based on an IBM PS/2 Model 60 computer and equipped with a Model 951 TGA and a Model 910 DSC units. The TGA data were obtained in flowing nitrogen at a heating rate of 10 °C/min whereas the DSC thermograms were obtained in nitrogen at a heating rate of 20 °C/min.

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Intrinsic viscosity [η] of the triblock copolymer was measured in dilute solutions in the range of 0.1-0.2 g/dL in methanesulfonic acid(MSA) at 30°C by using a Cannon Ubbelhode capillary viscometer.

Thin solid films of TBC-1 and binary blends of TBC-1 with 2,5-PBO were spin coated onto silica or indium-tin-oxide (ITO) coated glass substrates from their solutions in trifluoroacetic acid/methane sulfonic acid (v/v, 9:1). The films were subsequently immersed in ethanol solvent containing 1 wt% triethylamine to remove the acid and dried in a vacuum chamber at 60 °C. The film thickness of all samples was typically 100 nm and was measured by an Alpha Step Profilometer (Tencor Instruments) which has a resolution of 1 nm. Optical absorption spectra were recorded with a Perkin-Elmer Model Lambda 9 UV-Vis-NIR spectrophotometer. Steady state photoluminescence (PL), photoluminescence excitation (PLE), and electric field-induced PL quenching measurements were done on a Spex Fluorolog-2 spectrofluorometer equipped with a Spex DM3000f spectroscopy computer. The thin film samples for PL or PLE studies were positioned such that the emission was detected at 22.5° from the incident radiation beam. Relative PL quantum efficiencies were obtained by integration of PL emission spectra. For PL measurement under an external field, aluminum was evaporated onto thin film samples on indium-tin-oxide (ITO) coated glass. A positive bias voltage was applied to the ITO electrode, creating an electric field across the film sandwiched between ITO and aluminum electrodes.

The samples were illuminated through the ITO-glass side and the PL spectra collected under applied field. Picosecond time-resolved PL decay were performed using time-correlated single-photon-counting techniques.

Transient absorption spectroscopy was performed in a system which consisted of a Continuum PY61 Series Nd:YAG laser utilizing Kodak QS 5 as the saturable absorber to produce laser light pulses of ~25 ps FWHM. These output pulses were then amplified and the second and third harmonics generated (532 nm and 355 nm respectively). Dichroic beamsplitters in conjunction with colored glass filters were used to isolate the fundamental (1064 nm) and desired harmonic. The fundamental was directed along a variable optical delay and then focused into a 10 cm quartz cell filled with H_2O/D_2O (50:50) to generate a white light continuum probe pulse. The excitation and probe pulses (ca. 2 mm diameter) were passed approximately coaxially through the sample. The probe pulse was directed to a Spex 270 M monochromator through a Princeton Instruments fiber optic adapter and dispersed onto a Princeton Instruments dual diode array detector (DPDA 512). This allowed ~350 nm of the visible spectrum to be collected in a single experiment. A ST-121 detector controller/interface was incorporated into a 386/25 MHz PC to control the arrays and for data storage, manipulation and output. Additional experimental details, including the instruments and detailed methods used in our optical and photophysical experiments can be found elsewhere(18,19,27(a),27(c)).

Results and Discussions

Block Copolymer Structure and Composition. The synthetic approach used and the quantitative reaction yield ensured that the desired triblock copolymer structure was obtained. The molecular structures and composition of the copolymer TBC-1 (Figure 1) were established primarily by ^{1}H NMR and FTIR spectroscopies, thermal analysis, intrinsic viscosity, and various other spectroscopic measurements, as previously done for related polymers (18). The ^{1}H NMR spectrum of the triblock copolymer in CD_3NO_2/ $AlCl_3$ was essentially a superposition of those of the two parent homopolymers (HPBT, 2,5-PBO). The proton resonances of the 2,5-PBO blocks appear as a singlet at 9.25, a doublet at 9.0, and a doublet at 8.7 ppm, which are assigned to the protons *ortho, para,* and *meta* to the oxazole nitrogen, respectively. Two of the proton resonances of the HPBT block appear at 8.45 ppm (doublet) and 8.1 ppm, which are assigned to the 1,4-phenylene protons *meta* and *para* to the hydroxy group. The 1,4-phenylene proton *ortho* to the 2-hydroxy group also appears at 8.45 ppm, thus overlapping with the resonance of the proton at 6 position. The protons of the benzobisthiazole ring system of HPBT block appear as a broad resonance peak between 9.2-9.3 ppm, thus overlapping with the proton *ortho* to the oxazole nitrogen of 2,5-PBO block. The fact that the ^{1}H NMR spectrum of the TBC-1 is a superposition of those of the HPBT and 2,5-PBO homopolymers indicates that the copolymer is a true block copolymer. The ratio of the integrated peak at 8.7 ppm (2,5-PBO block) to that at 8.45 ppm (HPBT block) was 1.95, which is consistent with the theoretical ratio of 2 for the proposed block copolymer composition (Figure 1). The FTIR

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spectrum of TBC-1 exhibits all the characteristic bands of the parent homopolymers. There are major differences between the spectra of HPBT and 2,5-PBO, for example, the 958-cm^{-1} band due to heteroring breathing of HPBT, is absent in the 2,5-PBO spectrum whereas the C-O-C vibration band arising from the oxazole ring at ~1060 cm^{-1} is characteristic of 2,5-PBO. The ratio of the characteristic bands (958, 1060 cm^{-1}) was consistent with the composition of copolymer. The FTIR results in conjunction with the ^{1}H NMR spectra clearly confirmed the proposed structure and composition of the triblock copolymer.

Thermogravimetric analysis of the triblock showed a single onset of decomposition in N$_2$ (670 °C) that was different from either homopolymer, 650 °C for 2,5-PBO and ~700 °C for HPBT. Intrinsic viscosity of TBC-1 in methanesulfonic acid (MSA) at 30 °C was 2.5 dL/g which is higher than either the starting HOOC-B$_9$-COOH (1.0 dL/g) or a 2,5-PBO homopolymer with a degree of polymerization of 60(1.7 dL/g). All these results further confirmed the chemical linkage between the A and B blocks in the copolymer.

Exciton Localization Phenomena in Block Copolymer Thin Films. The expected exciton localization in a quantum-well heterostructure was probed in thin films of TBC-1 and its blends with 2,5-PBO by optical absorption spectroscopy. Figure 2 shows the absorption spectra of thin films of the pure TBC-1 and its binary blends with 2,5-PBO homopolymer. The optical absorption spectrum of 2,5-PBO homopolymer is also shown for comparison [The composition of TBC-

1/2,5-PBO blends is specified in terms of mole % HPBT repeat units, thus a 8 mol % blend corresponds to about 1:1 chain ratio(triblock to 2,5-PBO homopolymer) and 1 mol % corresponds to roughly one triblock chain in fourteen 2,5-PBO chains]. The highly structured absorption spectrum of TBC-1 is clearly a superposition of those of its two component homopolymers. The vibrationally resolved absorption bands in the 400-500 nm region with λ_{max} of 450 and 479 nm are characteristic of the HPBT block while the vibrationally resolved band in 240-380 nm region with λ_{max} of 270, 340, and 355 nm is due to 2,5-PBO block. The absorption spectra of the TBC-1/2,5-PBO blends are also superpositions of those of the two homopolymers, with varying ratio of the 479-nm band intensity, as expected. Compared to the optical absorption spectra of the homopolymer thin films, the absorption spectra of the copolymer and its blends reveal bandwidth narrowing and exciton peak sharpening. For example, the lowest energy absorption peak in 2,5-PBO (355 nm) is relatively more intense in the copolymer and its blends than in the homopolymer. Similarly, the 479-nm transition which is characteristic of the HPBT chromophore is more intense in the spectra of Figure 2 than previously reported for the homopolymer (24). The observation of the absorption bands characteristic of the component homopolymers in the absorption spectrum of the block copolymer is a strong evidence that excitons produced in the triblock chains are confined to two different spatial regions with different energy levels as schematically illustrated in Figure 1c. Exciton

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localization phenomenon revealed in the electronic absorption spectrum of the block copolymer is also an additional evidence of the block copolymer chain structure of TBC-1. However, no new optical transitions that could be attributed to quantum confinement effects was observed in the copolymer or blend absorption spectra. This is due to the low sensitivity of room temperature absorption spectroscopy in contrast to photoluminescence excitation spectroscopy which will be discussed subsequently. The sharpening of the exciton peak in the absorption spectra of the block copolymer and its blends may be an indication of reduced dimensionality of the excitons as has been observed in inorganic semiconductor quantum-well structures (*28*).

Quantum Confinement Effects. Photoluminescence excitation (PLE) spectroscopy at 298K was more sensitive in revealing evidence of progressive spatial confinement in going from the pure triblock to blends of the triblock with 2,5-PBO homopolymer. Figure 3 shows the PLE spectrum of the thin film of 2 mol% blend together with the thin film absorption spectrum of pure TBC-1 (normalized at 479 nm). The excitation spectrum was obtained by monitoring the blend thin film emission at 620 nm where there is negligible emission from the 2,5-PBO chromophore. The PLE spectrum of the blend has features similar to the absorption spectrum of the pure triblock as well as a major difference. The presence of a large 340-360-nm band due to 2,5-PBO absorption shows that the 620-nm emission from the HPBT block has a significant component in excitation energy transfer from 2,5-PBO. The major difference in the spectra of Figure 3 is

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that a small but entirely new band centered at 540 nm (2.3 eV) appears in the PLE spectrum. The new below gap 540-nm optical transition was dependent on the blend concentration and was only clearly seen in blends with low HPBT concentrations (<5mol%). Similar results were previously observed in other block copolymer/homopolymer blends, such as the TBA/2,5-PBO blends, where new optical transitions were seen below the band gap of PBZT(*19-22*). The new optical transition at 540 nm which is below the optical band gap of the lowest energy component of the block copolymer has not been anticipated in prior theoretical studies(*11-13*). Only optical transitions with energy levels intermediate between or higher than those of the two components of a block copolymer have been predicted. We propose that these below-gap excitonic states arise from spatial confinement induced delocalization of excitons along the length of the quantum boxes or wires ($0.35 \times 0.58 \times l_m$ nm^3, $l_m = 2.4\text{-}25$ nm) which is many times larger than the 1.3 nm bulk exciton Bohr radius of PBZT or HPBT (*23*). A net effect of such an exciton delocalization could be the formation of below-gap states much like the well-known photogenerated bipolaron/polaron states in conjugated homopolymers (*29*). Regardless of the exact quantum mechanical origin of the observed new optical transitions in the PLE spectra of these organic low dimensional systems, they are evidence of new exciton states induced by confinement in ultrasmall volumes.

Additional evidence of quantum confinement effects in thin films of the block copolymer /homopolymer blends was obtained through steady-state and time-resolved PL measurements as well as by electric field-modulated PL spectroscopy. Figure 4a shows the PL emission spectra of thin films of TBC-1 and TBC-1/2,5-PBO blends excited at 360 nm. Excitation at 360 nm preferentially excites 2,5-PBO, as can been seen from the absorption spectrum of Figure 2. Excitation of TBC-1 at 360 nm results in a broad PL emission band in the 460-640 nm region with a dominant peak at 566 nm and a shoulder at 495 nm. Similar PL emission spectra of TBC-1 were obtained when the HPBT block was directly excited at either 450 or 479 nm where the 2,5-PBO block does not absorb. The broad, featureless PL emission spectrum of the block copolymer TBC-1 is very similar to that of the HPBT homopolymer (λ_{max} =570 nm) which has been previously assigned to excimer emission (24). This similarity of emission spectra of HPBT and TBC-1 suggests that microphase separation has occurred in the TBC-1 block copolymer and thus that its luminescence was from excimer-forming aggregates or microdomains. Independence of the block copolymer PL emission spectrum from excitation energy and the nearly complete quenching of emission from 2,5-PBO block in the 380-420 nm region indicates that there is efficient excitation energy transfer from 2,5-PBO blocks to the middle HPBT block and also that the lower energy HPBT block acts as a potential well which traps excitons and serves as a radiative recombination center.

The PL emission spectra of thin films of the binary block copolymer (TBC-1) /homopolymer (2,5-PBO) blends of varying composition are also shown in Figure 4a. The blend PL spectra are dramatically different from that of the pure block copolymer in three ways: the emission band spectral position, the PL emission lineshape, and the Stokes shift of the emission maximum from the absorption maximum. As the block copolymer content of the blends, as measured by mol% HPBT, is progressively reduced to 2%, the HPBT block emission maximum is blue shifted to 479 nm. In the dilute blends (<6%), a vibrationally resolved PL emission spectrum is observed. The emission linewidth in terms of full width at half maximum (FWHM) is reduced from 144 nm (571 meV) for the 15% blend to 47 nm (280 meV) for the 2% blend. The Stokes shift of the PL emission is reduced from 413 meV for the block copolymer to only 11 meV for the 2% blend. Furthermore, the blend emission spectra shown in Figure 4a were independent of excitation wavelength. The progressive evolution of the spectrally narrow and vibrationally resolved PL emission spectrum of the dilute (2%) blend from that of the microphase separated copolymer reflect the increasing spatial confinement of the HPBT blocks and emergence of the isolated potential well as exciton traps and radiative recombination centers. Since the Stokes shift in conjugated polymer and molecules commonly arises from excitation relaxation, the relatively small Stokes shift in the PL emission of dilute blends indicates that excitons photogenerated in the HPBT blocks are confined to the lowest energy exciton states.

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The blend PL emission spectra in Figure 4a also show the progressive increase of the 2,5-PBO emission centered at ~380-400 nm with decreasing concentration of HPBT. Although there is nearly complete quenching of emission from the 2,5-PBO chromophores in the pure triblock and in the 12-15 % blends, further dilution results in increased emission from the predominantly 2,5-PBO-containing blends because of the reduction in the number of HPBT blocks which act as luminescence quencher for excited 2,5-PBO. The highly efficient excitation energy transfer from the excited 2,5-PBO blocks to HPBT blocks is thus regulated by the composition of the blends.

The observed PL emission spectral change in the block copolymer /2,5-PBO blends was accompanied by enhancement in PL quantum efficiency with increasing HPBT block confinement as shown in Figure 4b. About a factor of 4 enhancement in PL quantum yield was observed in going from the pure TBC-1 triblock (18.4 mol% HPBT) to 0.5 % blend. The enhancement with increasing spatial confinement of HPBT blocks can be understood to arise from a decrease in the nonradiative recombination rate with HPBT chromophore dilution in the blends. This interpretation was confirmed by the results of picosecond-resolved PL decay dynamics study which showed an increase in lifetime or decay time with decrease in HPBT block concentration. The decrease of nonradiative recombination rate with decreasing concentration of HPBT blocks in the blends in turn is a consequence of the progressive elimination of the bimolecular

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recombination component of nonradiative decay as the distance between the HPBT blocks is increased.

The results of electric field-modulated PL spectroscopy on ca. 100-nm thin films of pure TBC-1 and its 3% blend are shown in Figure 5 for 450-nm excitation. Up to 50% quenching of the photoluminescence of the pure block copolymer is observed at an applied bias voltage of 12 (Figure 5a) which corresponds to an electric field of 1.2×10^6 V/cm. This large electric field-induced quenching of photoluminescence in a block conjugated copolymer is similar to previous observation on conjugated homopolymers by our laboratory (*19*) and others (*30*). The electric field-induced quenching of luminescence arises from field-induced dissociation of excitons in the materials and the extent of dissociation depends on exciton binding energy, spatial confinement, and electric field. In contrast, electric field-induced quenching of luminescence was not observed in dilute blends, such as the 3% blend shown in Figure 5b, at electric fields of up to 2.5×10^6 V/cm. This exceptional stability of excitons in HPBT quantum boxes under large electric fields reflects their strong three-dimensional confinement and large binding energy.

Stimulated Emission From Block Copolymer Heterostructures. Transient photoinduced absorption (PA) spectroscopy with picosecond time resolution was done on a different block copolymer /homopolymer blend system (TBA-1/2,5-PBO) which is related to the present TBC-1/2,5-PBO blend system (see Figure 1). This experiment is essentially a pump- and -probe technique in which a 12

mol% TBA-1/2,5-PBO blend thin film with optical density of 0.6 at 470 nm was photoexcited at 355 nm and then the excited state was probed with white light continuum (400 - 950 nm). Figure 6 shows transient absorption spectra at selected delays after photoexcitation. No transient species was observed at 0 ps delay. However, photoinduced bleaching in the 380 - 490 nm region with peaks at 440 and 470 nm was observed at t > 0 ps delays. Since the spectral position of photobleaching overlaps with the absorption band of PBZT blocks in TBA-1, it can be clearly identified as the bleaching of PBZT chromophores. Photobleaching of the PBZT absorption reached its maximum with an optical density of -0.12 at 470 nm at 100 ps delay. At subsequent delay times (100-200 ps, Figure 6) the photobleached signal progressively decays. Similar PA experiments on the pure homopolymer thin films (2,5-PBO thin film with an optical density of 2.0 at 355 nm and PBZT thin film with an optical density of 0.6 at 470 nm) photoexcited at 355 nm showed that photobleaching in PBZT reach a maximum at 50 ps delay with an optical density of -0.015 at 470 nm. No photoinduced absorption signal in the 400-700 nm was observed in 2,5-PBO at all delay times, although occurrence of PA below 400 nm, which was not probed, cannot be ruled out. These results show that the 12 % blend thin film which has an identical optical density as the PBZT homopolymer thin film exhibits an enhanced photobleaching by a factor of 8 compared to the homopolymer. The dramatically enhanced photobleaching in the ABA/A block copolymer blend is a consequence of the efficient excitation energy transfer from A* to the middle B block.

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Stimulated emission (SE) in the 490 - 700 nm region, which coincides with the emission region of PBZT (*18-20*), was also observed in the PA spectra of the 12% copolymer blend thin film as shown in Figure 6. The large SE signal at 100 ps delay in the 500-520 nm region with an optical density of -0.08 corresponds to an optical gain of 20%. The SE signal persists to 200 ps (Figure 6). SE signal of any magnitude was not observed in either 2,5-PBO or PBZT homopolymer. Clearly, the observed efficient stimulated emission in the TBA-1/2,5-PBO blend is a direct result of excitation energy transfer from the excited 2,5-PBO to the PBZT blocks in the copolymer.

The dynamics of the PA in the block copolymer blends revealed that whereas the photobleaching occurred instantly (<1 ps) after photoexcitation, there was about 80 ps risetime for the stimulated emission. Given the high excitation density of 100 mJ/cm^2 and the large A absorption cross section in the ABA/A blends, the excited state energy level of A will be significantly populated by the pump pulse. Since excitation energy transfer occurs on the subpicosecond time scale (*31*), the observed instant photobleaching of the B can be understood. The observed risetime of SE is explained by the fact that SE occurs only when the population of B is inverted by energy transfer and accumulation of B in the excited state. Blend thin films of various TBA-1/2,5-PBO compositions were investigated under similar PA experimental conditions to gain more insight into the factors that control SE in these materials. Enhanced photobleaching was observed in all the blends. However, significant SE was only observed in blends of 3-15

mol% PBZT but not in the more dilute (< 3%) or more concentrated (> 15%) blends. These results suggest that a balance between spatial confinement and chromophore concentration is essential to achieving population inversion and efficient stimulated emission in block copolymer heterostructures.

Conclusions

A new symmetric ABA triblock conjugated copolymer, poly(2,5-benzoxazole)-*block-* poly(benzobisthiazole-2-hydroxy-1,4-phenylene)- *block* -poly(2,5-benzoxazole), has been prepared and thin films of its blends with the higher energy gap 2,5-PBO homopolymer have been shown by photoluminescence emission and excitation, electric field-modulated photoluminescence, and picosecond absorption spectroscopies to exhibit a range of quantum confinement effects at room temperature. Some of the observed quantum effects include a new optical transition in the photoluminescence excitation spectrum, enhanced luminescence efficiency, PL emission spectral narrowing, and unusual exciton stability in large applied electric fields. However, thin films of the pure block conjugated copolymer did not exhibit any quantum size effects because of microphase separation. These new HPBT-based block copolymer quantum-well heterostructures thus expand the rather small number of currently known organic quantum wires and quantum boxes.

Cooperative interaction between the two electroactive and photoactive components of the block copolymer/homopolymer (ABA/A) blends is

exemplified by the efficient excitation energy transfer from A to B which led to the observed enhanced photobleaching and large stimulated emission. Block conjugated copolymer/ homopolymer blends thus represent a promising novel class of solid state lasing materials.

Acknowledgments

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Figure Captions

Figure 1. (a) Chemical structures of ABA block conjugated copolymers and parent homopolymers. (b) Schematic illustration of triblock copolymer chain. (c) Schematic illustration of quantum-well formation in ABA triblock chain due to electronic structure differences.

Figure 2. Optical absorption spectra of thin films of the triblock/homopolymer (TBC-1/2,5-PBO) blend system. Blend composition in mol% HPBT repeat units is shown.
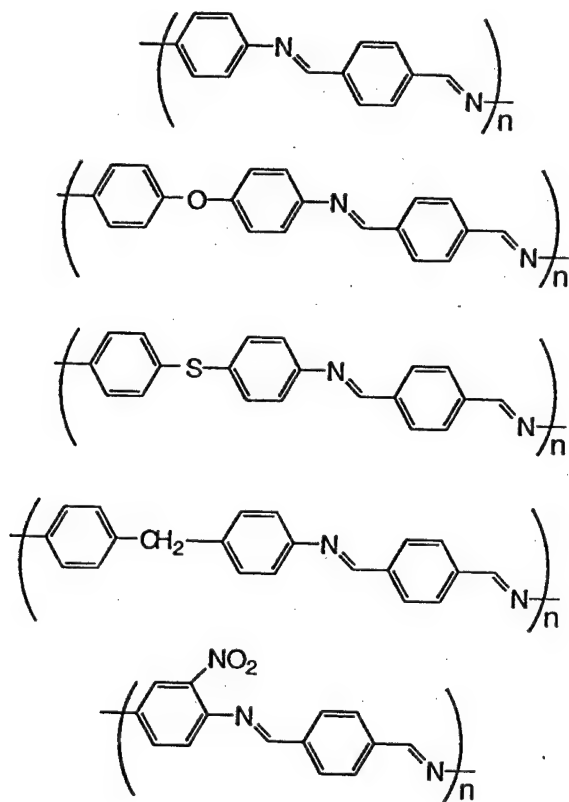
Figure 3. Room temperature (298K) PL excitation spectrum (620-nm emission) of the 2% blend thin film along with the absorption spectrum of TBC-1 thin film. The PLE and absorption spectra were normalized at 479 nm. Vertical arrow marks a new optical transition.

Figure 4. PL emission spectra of TBC-1/2,5-PBO blend system thin films at 298K. (a) PL emission spectra (360-nm excitation) as a function of blend composition. (b) Relative PL quantum efficiency as a function of blend composition for the blend spectra in (a) and excitation of 450 nm.

Figure 5. Electric field-modulated PL spectra of thin films of TBC-1 (a) and 3% blend (b) for 450-nm excitation at different bias voltages.

Figure 6. Transient absorption spectra of 12 mol% TBA-1/2,5-PBO blend thin film recorded at selected delay times after a 355-nm laser excitation: (a) 100, (b) 130, and (c) 200 ps.
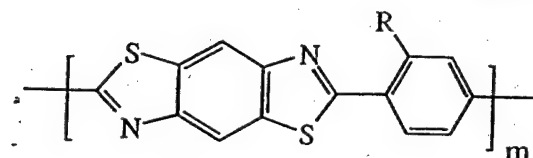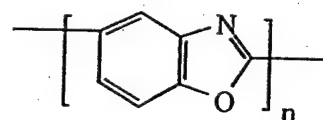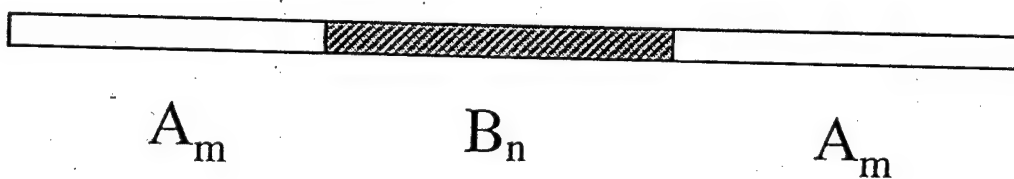
Chart 1

Fig. 1
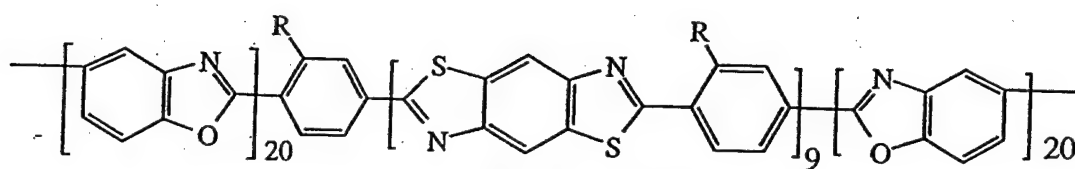
a.

TBA-1, R=H
TBC-1, R=OH
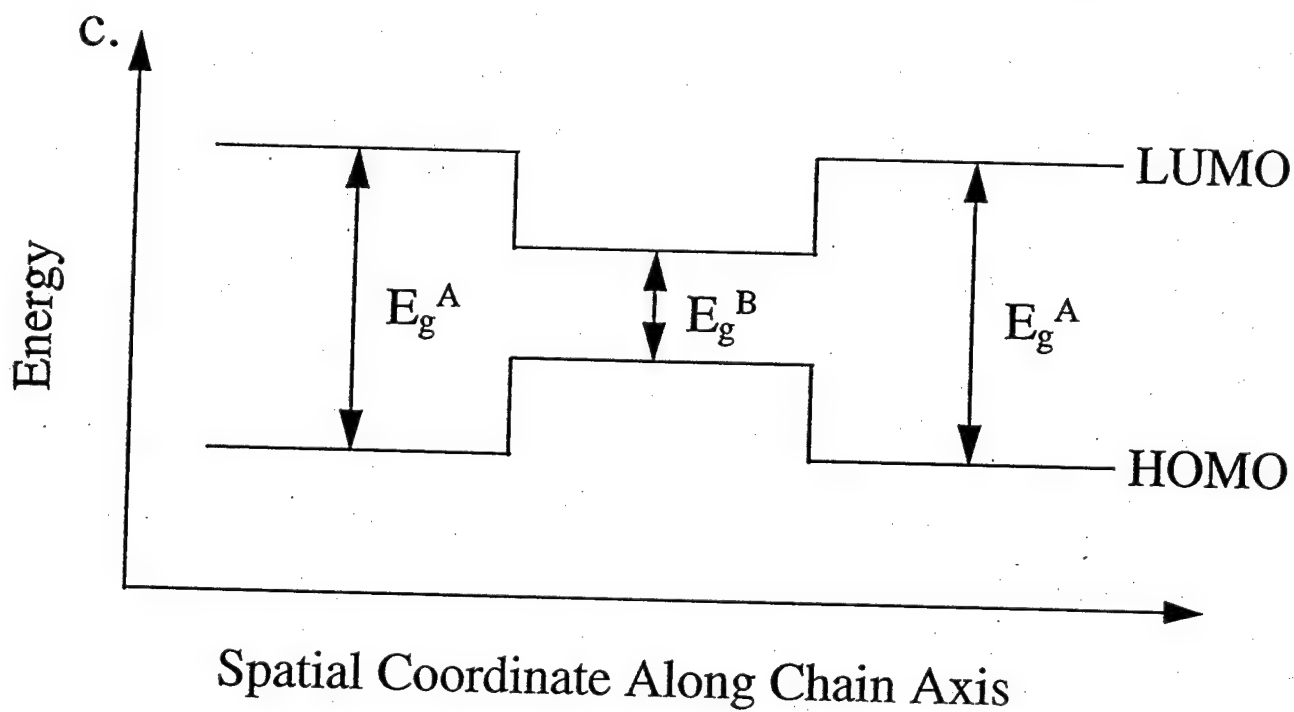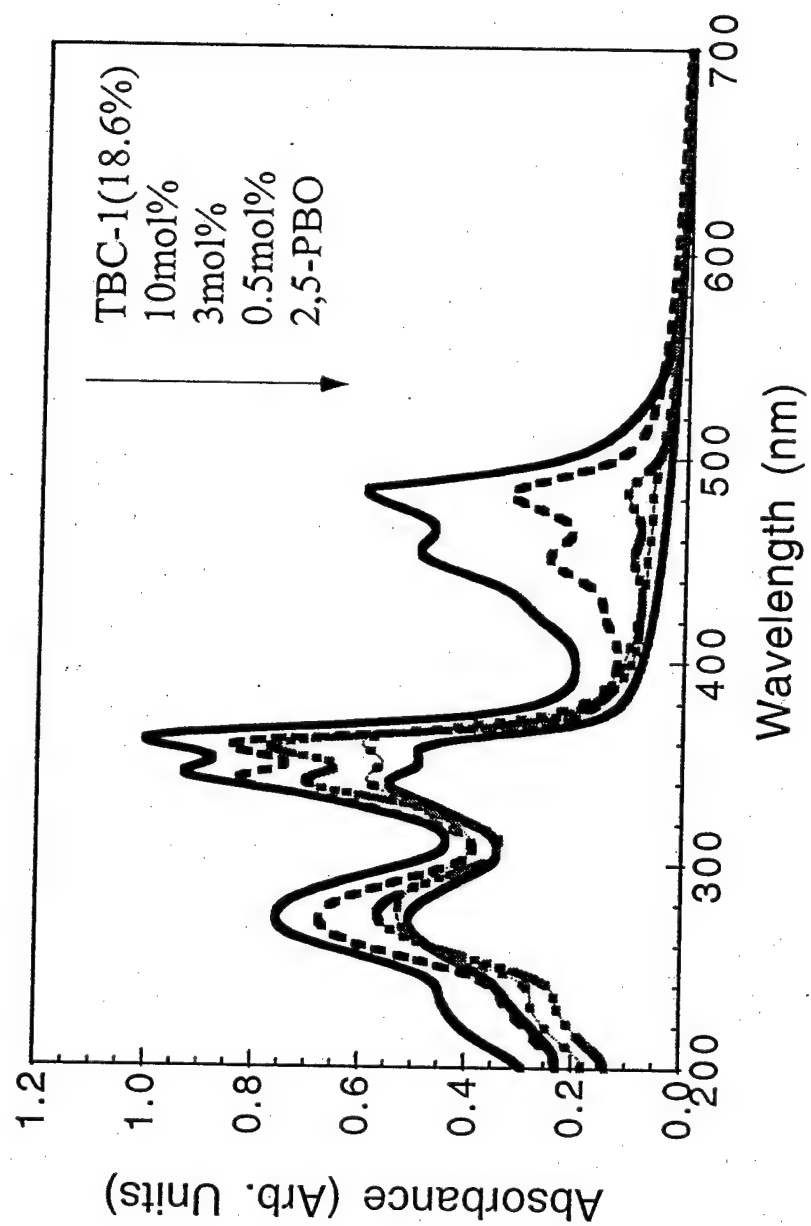
PBZT, R=H
HPBT, R=OH

2, 5-PBO

b.

A_m B_n A_m

c.

Energy

LUMO

E_g^A E_g^B E_g^A

HOMO

Spatial Coordinate Along Chain Axis

Fig. 2

TBC-1(18.6%)
10mol%
3mol%
0.5mol%
2,5-PBO

Wavelength (nm)

Absorbance (Arb. Units)

Fig. 3

PLE Intensity (Arb. Units)

PLE (2% TBC-1)
UV-Vis (TBC-1)

Wavelength (nm)

Absorbance (Arb. Units)

Fig. 4

Fig. 5

Fig. 6